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FOR LIQUID PROPELL (U) ARMY BALLISTIC RESEARCH LAB
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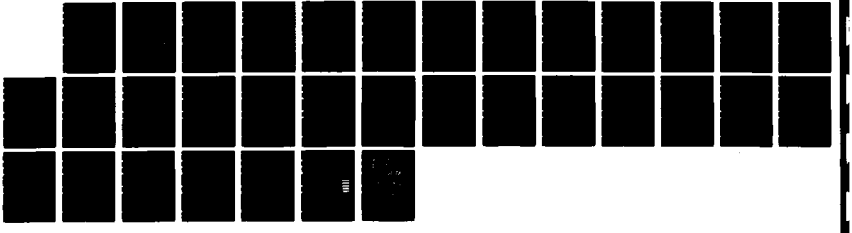

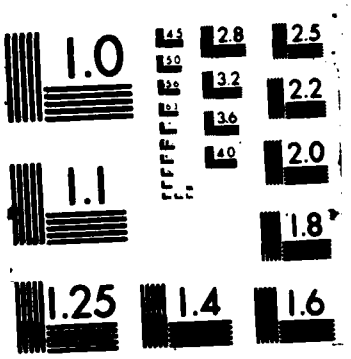
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TECHNICAL REPORT BRL-TR-2837

DSC STABILITY TEST FOR LIQUID PROPELLANTS: A PRELIMINARY REPORT

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ROBERT A. FIFER
PAMELA J. DUFF

SEPTEMBER, 1987

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US ARMY BALLISTIC RESEARCH LABORATORY
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The use of a Differential Scanning Calorimeter (DSC) for monitoring the stability of HAN-based liquid propellants has been investigated. Preliminary experiments have been complete which establish criteria for obtaining reproducible initiation temperatures (T_{in}). Careful control of sample size (volume), inert sampling materials and operation at elevated pressur have yielded definitive T_{in}s with the lowest standard deviation. Results for 1845 in aluminum pans at 6.9 MPa yielded an average T_{in} of 120°C and standard deviation of 4°C, while an average T_{in} of 124.8 and standard deviation of 2.4 was obtained for 13 M HAN in th presumably more inert tantalum pans at a somewhat lower pressure (5.2 MPa). Thus, it appears that with further refinement the T_{in} values obtained in such a DSC experiment can b successfully used to monitor the relative stability of HAN-based propellants. The T_{in} values obtained reflect initiation under the DSC conditions with small samples; no extrapolation to the ignition temperature of bulk HAN-based propellant under other conditions is attempted.

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I. INTRODUCTION

The relative stability of HAN-based liquid propellants under varying conditions of purity and age has previously been indeterminable. The initiation temperature of HAN as a function of concentration has been studied[1] and the conclusion was that the initiation temperature varies inversely with concentration and that the initiation temperature for 11 Molar nitrate is the same as for 11 Molar HAN. Several studies on the thermal decomposition of HAN-based LPs have also been reported, however, these have focused on decomposition temperatures of selected HAN mixtures (e.g., HAN spiked with metals[1] or HAN with 4-carbon amines[2]). In both of these cases a 50 cc AMINCO bomb equipped with thermocouples was used to measure initiation temperatures. The bomb had also been used earlier[3] to determine decomposition gases of various HAN solutions in an attempt to derive rate equations. However, no test has yet been developed which can determine the relative stabilities of liquid propellants. This type of information could be quite useful, for example, in monitoring the shelf life of the propellant, or any contamination, degradation etc.

The paper describes the initial attempts to use a DSC to develop a stability test for liquid propellant materials. A second paper has been written[4] in which results from this preliminary work are incorporated into the further development of a DSC test in which the effect of trace metals on liquid propellant stability is determined.

II. EXPERIMENTAL

All experiments were run on a Perkin Elmer (PE) DSC-4 equipped with a System 4 microprocessor controller, digital "interface" (Analog-to-Digital converter), and Model 3600 "data station" (microcomputer) operating with PE's thermal analysis software. As recommended for decomposition studies, a "flow-through" cover plate was used in place of the standard cover plate. When it became clear during the course of this study that pressure operation was required, the DSC was modified for operation at up to 6.9 MPa (1000 psi). Since the chambers surrounding the sample and reference holders, and the electrical feedthroughs into them, were already capable of withstanding these pressures, the primary structural modification was the addition of a removable hold-down assembly for the flow-through cover plate, secured via connecting rods to a second plate mounted on the underside of the DSC head. Further modifications to this system have been subsequently made.[4] Flow rates were generally about 50 cc/min. Argon, commonly used as the purge gas in DSC experiments, could not be used at high pressure in this DSC since it resulted in very noisy, erratic baselines, presumably due to thermal fluctuations in the high density gas flowing around the sample holders. Switching to helium for high pressure operation completely eliminated this "noise" problem, presumably due to its much higher thermal conductivity.

The samples investigated consisted of 13 Molar hydroxylammonium nitrate (HAN), and the propellants NOS-365 and BRL-1845. Many different types of sample containers were used, including pierced or unpierced standard aluminum PE "volatile" DSC pans, PE stainless steel high pressure (6.9 MPa, or 2000 psi) capsules, as well as PE gold pans, custom-made tantalum pans, and aluminum pans onto which was sputtered a coating of platinum [illegible]. In addition,

stainless steel HPLC tubing and glass capillary tubing were used. These and other containers are discussed in more detail in the following section. Typically, depending on the sample configuration, about 2 µl (~3 mg) propellant samples were used. In order to achieve reproducible (e.g., ±5%) sample sizes, these were measured out with a 10 µl Hamilton #701 syringe, and weighed to ±0.01 mg.

III. RESULTS

When we began this task, we thought it would be a relatively simple matter to design a DSC stability test for liquid propellants, and then use it to study the effects of metal impurities, complexing agents, etc. This turned out not to be the case. The HAN-based liquids behave very non-reproducibly under standard DSC conditions. A couple of hundred experiments have been performed, with many different configurations, conditions, sample holder materials, etc. The following is a roughly chronological account of some of the preliminary techniques tried in an attempt to achieve reproducible initiation temperatures (T_{in}) in the DSC. The purpose of describing this earlier work is not just to emphasize the difficulty we encountered in developing a usable DSC test, but to point out some of the many interesting but as yet unexplained phenomena we discovered in the course of the investigations--phenomena that will undoubtedly have more meaning when further information becomes available about the kinetics and mechanisms of the decomposition/initiation processes.

A. Atmospheric Pressure in Metal Containers

Under "standard" DSC conditions (programmed heating at 1-10 deg/min in pierced aluminum pans at atmospheric pressure), the propellants produce very erratic results, as shown in Figure 1. The shape of the thermogram is different for almost every experiment (Table 1). There are frequently multiple exotherms, and the temperature of the first exotherm varies over a large temperature range (e.g., 120-160°C, see Table 1A). The multiple exotherms are presumably due to boiling and splattering of the propellant. Endotherms often, but not always, precede the exotherms. In order to compare the reproducibility of the T_{in} values within each treatment it is useful to calculate an average T_{in} value and corresponding standard deviation. However, in this instance there is no single T_{in} for each run, so such a calculation is meaningless.

HAN is a reactive acidic salt and its reactivity towards various metals is well known.[3] However, at the time that this work was performed it was suspected, although not definitively shown, that HAN reacts with Al. (Since then a report has been published which confirms the reactivity of HAN and Al.)[5] In order to assure that this erratic behavior was not due to surface-related effects, experiments were carried out in aluminum pans coated with gold or platinum.

The results under these conditions were only slightly improved. In most cases only a single exotherm was generated, although in several instances multiple peaks were still obtained (Figure 2). The endotherms which often preceded the major exotherms in the case of Al pans were eliminated. The initiation temperature (T_{in}) was not uniform however, and varied over a temperature range of 70-180°C, with an average value of 129°C and standard

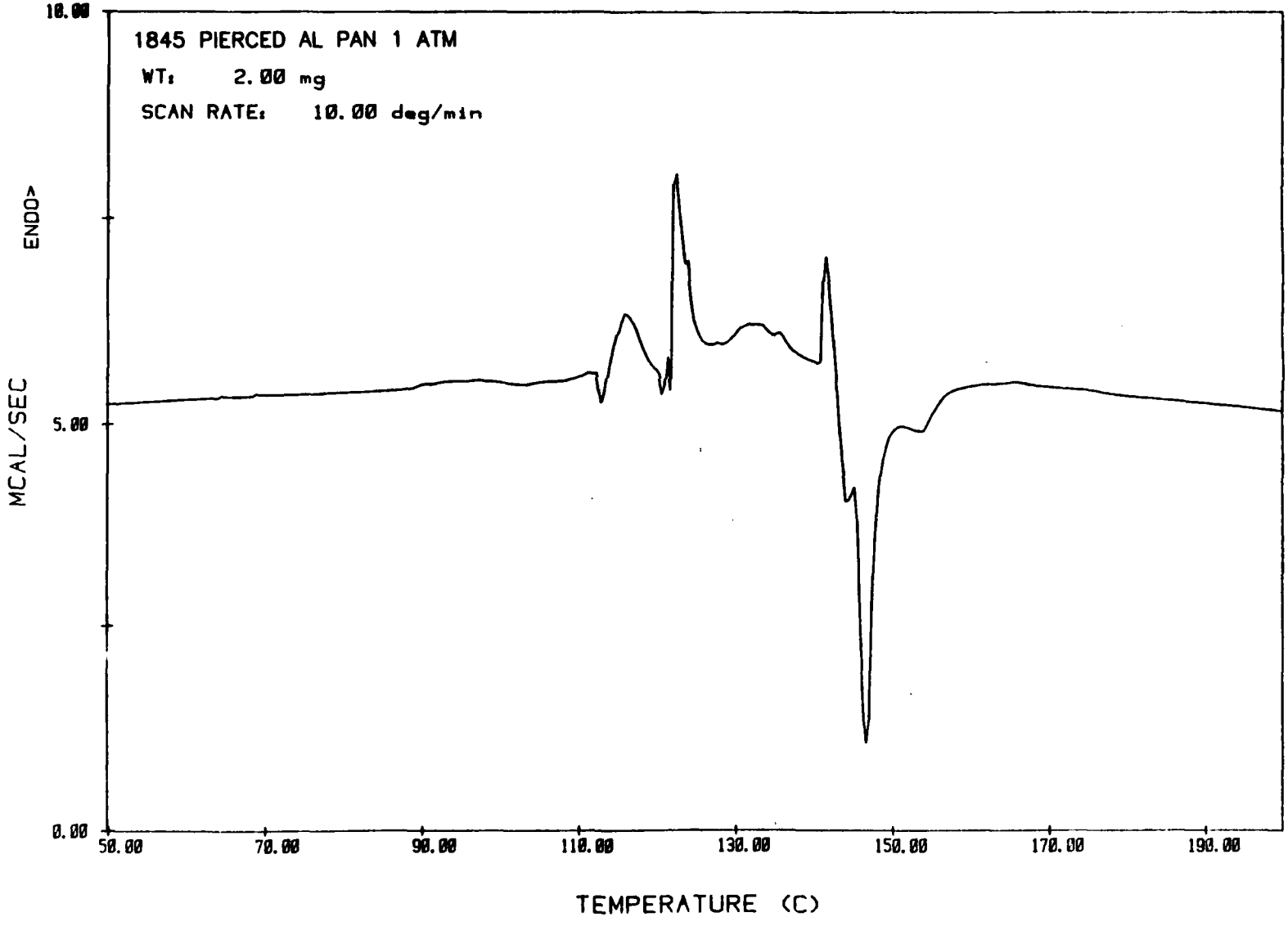

Figure 1. Thermogram for 1845 in Pierced Aluminum Pans at 1 Atmosphere, Showing Erratic and Non-Reproducible Behavior Under Standard DSC Conditions

Table 1. Major Endo- and Exotherms for Various HAN-Based Samples

A. Atmospheric Pressure

Sample/Size* (mg)	Endotherms (C)	Exotherms (C)	Comments
Aluminum Pans			
3.3	134	151,155,158	Multiple exotherms; no
3.9	84,122	97,108,136	average T_{in} or std. dev.
7.6		138,140,157	obtained
14.71	149	174	
Coated Pans			
Au 4.2[a]		86	Endotherms eliminated
1.0		63	Single exotherm obtained
5.8		178	in most cases
3.8		177,197	Large scatter in T_{in};
Pt 3.2		140	T_{in}=128.8, σ=52.5
2.4		6.7 min[b]	
Stainless Steel Tubing			
1.0	117,126,143	146,153	Multiple peaks, probably
1.0		153,157	due to degassing of sample
1.2	119,125	126,142,153	Multiple exotherms; no
1.0	98,102	103,109	average T_{in} or std. dev.
1.0	76	82,88	estimated
Substrates in Al Pans			
Molecular sieve, 3.2		141	Single exotherm obtained,
Glass wool, 2.9		186	probably due to elimination
Porapak, 7.4		154	of splattering
Silica, 2.2		116	Std. dev. is high;
Silica Gel, 3.3		130	T_{in}=144.5, σ=23.9
Zirconium powder, 2.9		109	T_{in} significantly lower
Aluminum powder, 7.4		85	
Fiberglass, 2.6		120-185	Broad exotherm

Table 1. Major Endo- and Exotherms for Various HAN-Based Samples (Cont'd)

B. Elevated Pressure

Sample/Size* (mg)	Endotherms (C)	Exotherms (C)	Comments
0.76 MPa			
3.3		169	Single exotherms obtained
3.1		148	
3.3		30 min[b]	
2.4		8 min[b]	
NOS 2.0		96	Single exotherm obtained
NOS 3.0		124	Std. dev. is high;
NOS 3.6		132	Average T_{in}=138.3, σ=2.4
NOS 3.9		187	
NOS 2.9		142	
5.2 MPa/Ta pans			
3.1		123	Single exotherms obtained
3.2		125	Std. dev. is greatly
3.2		123	improved; Average
3.2		128	T_{in}=124.8, σ=2.4
5.2 MPa/Al pans			
3.2		119	Single exotherms obtained
3.2		157	Std. dev. is high;
3.2		104	Average T_{in}=126.6, σ=22.3
6.9 MPa			
1845 2.9		120	Single exotherms obtained
1845 2.9		116	Std. dev. is greatly
1845 3.0		118	improved; Average
1845 3.0		127	T_{in}=120, σ=4.0
1845 3.0		117	
1845 3.1		122	
HAN 3.0		154	Single exotherms obtained
HAN 3.0		126	Std. dev. is high;
HAN 3.0		124	T_{in}=133.2, σ=20.2
HAN 3.0		153	
HAN 3.1		125	
HAN 3.1		100	
HAN 3.1		124	
HAN 3.2		114	
HAN 3.2		150	
HAN 3.2		162	

*Unless stated otherwise, all samples were HAN, run at 10 C/min
a - 1 C/min
b - Isothermal

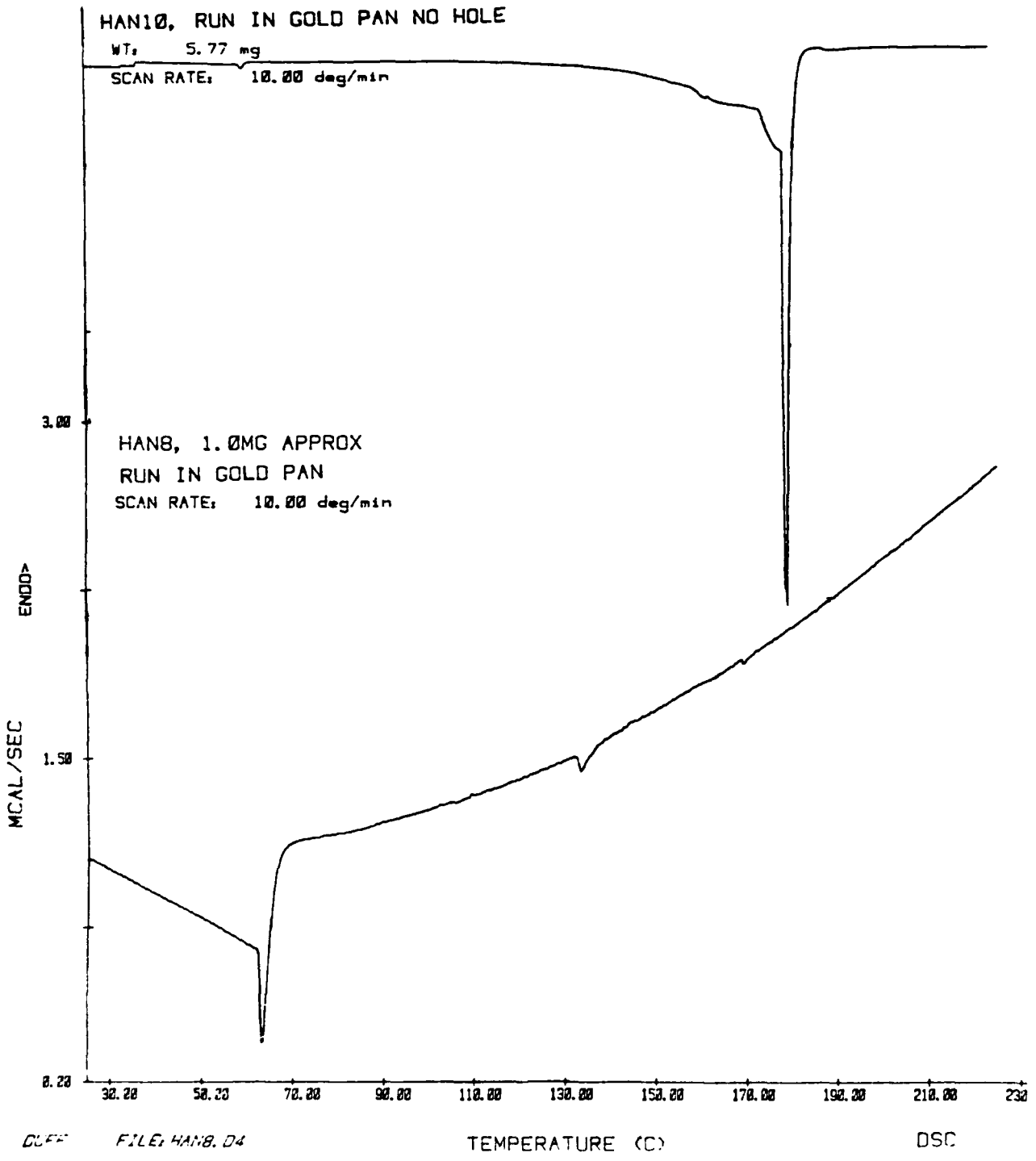

Figure 2. Representative Thermograms of HAN in Au Pans, Showing the Absence of Pre-Endotherms and Improved Peak Shape as Well as the Range of Temperatures over which the Major Exotherm (T_{in}) Occurs

deviation of 52.5°C for the Au coated pans (Table 1A). Although the pans appeared completely and uniformly coated, after heating the coating usually looked a bit distorted and occasionally even [illegible] it is quite possible that HAN reacts with the Al during the time of experiments (typically about 15 minutes). The blistering of the Pt and Au plating also suggests reaction between the Al and HAN. Thus, the possibility exists that Au or Pt might be suitable materials and more effective for obtaining reproducible results if an improved coating procedure for pans constructed of Au or Pt were used.

A number of experiments were carried out with the propellant on a powdered (or fibrous) substrate. The rationale was that the powdered substrate would prevent the sample from splattering during heating, and possibly act as a "thermal sink" for the exothermic energy released, thereby inducing slower, more controlled decomposition.

Non-metal and typically inert powders such as molecular sieve, silica gel, Porapak Q, amorphous silica and silica powder all gave a single, sharp exotherm, indicating that the splattering observed in Al pans with no substrates had been diminished (Figure 3). This was true even though only the first two materials were wetted by the propellant, and is probably attributable to the matrix breaking up the dissolved gases in a manner similar to boiling chips. When deposited over relatively large quantities of zirconium or aluminum powders, the HAN trickled freely between the particles. In these samples, lower reaction temperatures were observed (~100°C), possibly due to catalytic effects and/or greater thermal conductivity of the powdered metals (Figure 3). However, in these instances, the sample pans were filled to a greater extent than in the preceding examples and perhaps the volatiles trapped above the sample promoted further decomposition. The aluminum-substrate sample, run with solid lids and therefore having the potential to self-pressurize, did, in fact, exhibit the lowest decomposition temperature in this series. After the experiment with the aluminum substrate, it was observed that the top was blown off and the sample flipped over; thus, the shape of the exotherm is not entirely representative of HAN decomposition. Little evidence was observed that the matrices provided a heat sink and promoted slow reaction; in fact, rather sharp, regularly shaped peaks were obtained. It may be that the matrices (fairly good insulating materials) are heated thoroughly in the DSC and once this heat is absorbed, act as a source of heat. Thus, once the reaction of the HAN begins, thermal energy is available in the surrounding matrix particles to sustain it and the reaction proceeds rather quickly.

Slow reaction did occur (several minute duration) in samples drawn by capillary action into tightly-packed fiberglass fibers (Figure 3). In these samples individual HAN molecules are more likely to be adjacent to the matrix than in previous samples in which the HAN was deposited over the powders and in some cases did not even wet them. It might be possible for HAN at one site in the fiberglass bundles to react independently of HAN at a distant site, resulting in decomposition over a longer period of time.

These experiments showed that it was possible to reduce the effects due to spreading and splattering. However, reproducible decomposition temperatures were not achieved, and results ranged from about 120-190°C for the non-metal powder substrates, with an average temperature of 144.

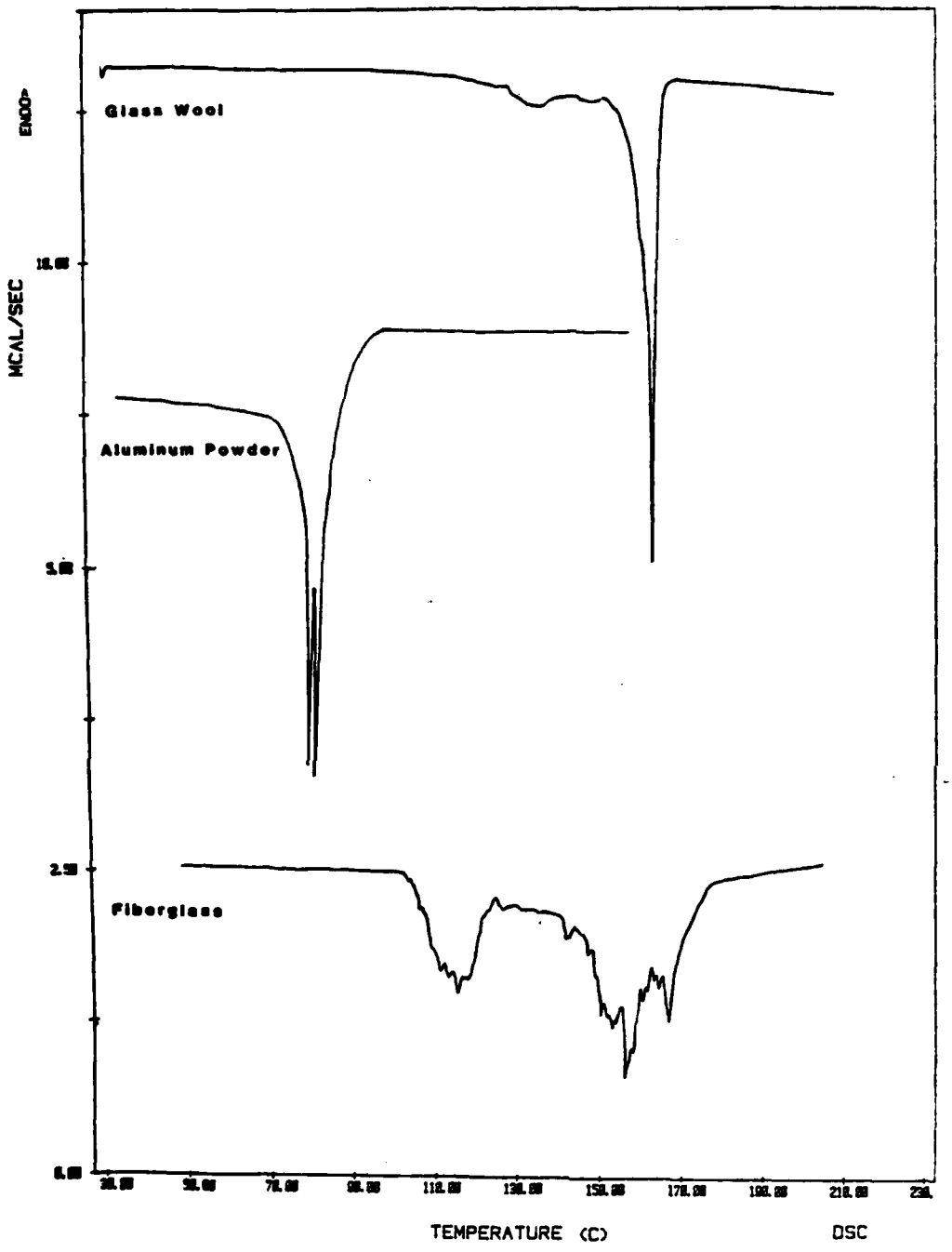

Figure 3. Thermograms Showing the Absence of the Pre-Endotherms for Samples in Aluminum Pans with Substrates. The Most Definitive T_{in} is Obtained Using an Inert Substrate (e.g., Glass Wool) in Which the Propellant is not Totally Absorbed by the Substrate

(Table 1A). The variance was an unacceptably high 21.8°C, indicating that the reactions resulting in the release of gas from the samples is not reproducible. This may, in part, be due to the fact that these samples were run in Al pans and the reactivity of the Al with HAN would not be expected to be reproducible. Also, it is assumed that the substrates, mostly molecular sieve chromatographic packings and inert to most compounds, are also inert to HAN. If this were not true, such substrate-HAN interactions could add to the irreproducibility. Additional factors may be variations in the loading of both the HAN and substrates, but the major factor was believed to be water vaporization which was not sufficiently reduced in these treatments. It should be noted that the rather fast reactions under these conditions yield peaks with regular shapes, not unlike results obtained for solid propellant materials such as the nitramines.[6] Since the purpose of this work is ultimately to correlate changes in decomposition between samples of different composition (e.g., variations in formulation or impurities and/or degradation), sharper peaks allow smaller changes in decomposition temperature to be observed.

B. Confined (Self-Pressurizing) Samples

Since the suppression of water vaporization/boiling is probably necessary to achieve reproducible decomposition or initiation, several techniques were tried that involved self-pressurizing sample containers. The disposable PE "volatile" aluminum pans that were used (pierced) in the experiments described above have a diameter of about 3 mm, a volume of about 20 microliters, and a rated pressure of a few atmospheres. Samples of propellant (~3 mg) heated in sealed (unpierced) pans give somewhat less erratic results than with the pans pierced, with fewer exotherms and perhaps a somewhat higher decomposition temperature, but the results are still too non-reproducible to be of use. The results were similar with the stainless steel or gold-plated stainless steel PE 45 microliter reusable screw-top "high pressure capsules", which have a pressure rating of 15 MPa (2175 psi). Such pressures should be quite effective in suppressing vaporization and boiling; the problem is that vaporization and boiling are not sufficiently suppressed at the low loading densities that must be used to prevent damage to the capsule or DSC. (On a larger scale, this applies to previous heatable closed bomb work as well.)

One technique was tried that did involve "total confinement" (no initial free volume). Propellant was drawn upward through a length of cleaned and propellant-treated small bore (0.38 mm, or 0.015 in i.d.) stainless steel HPLC tubing. A number of short (4-5 mm) sections of tubing were then crimped off with heavy-duty wire-cutting pliers. Experiments with the HPLC pump (using a solvent, not propellant) showed that the ends crimped-off in this manner had a rupture pressure greater than the maximum pressure of the HPLC pump (41 MPa, or 6000 psi). The sections of tubing were run directly in the DSC sample holders (no sample pan). Although difficult to see visually, post-run weighing confirmed that the tubing did, in fact, rupture upon initiation. Despite the confinement, the results for several samples were no more reproducible than for the sample pan experiments. Often the curves showed rather jagged endotherms and exotherms, possibly due to degassing which might occur at the high pressures generated in the stainless steel tubing (see Figure 4, Table 1A). This precluded the calculation of a meaningful average value of the T_{in} and variance. However, several samples run a day after being loaded in the tubing gave different results from those of the day before,

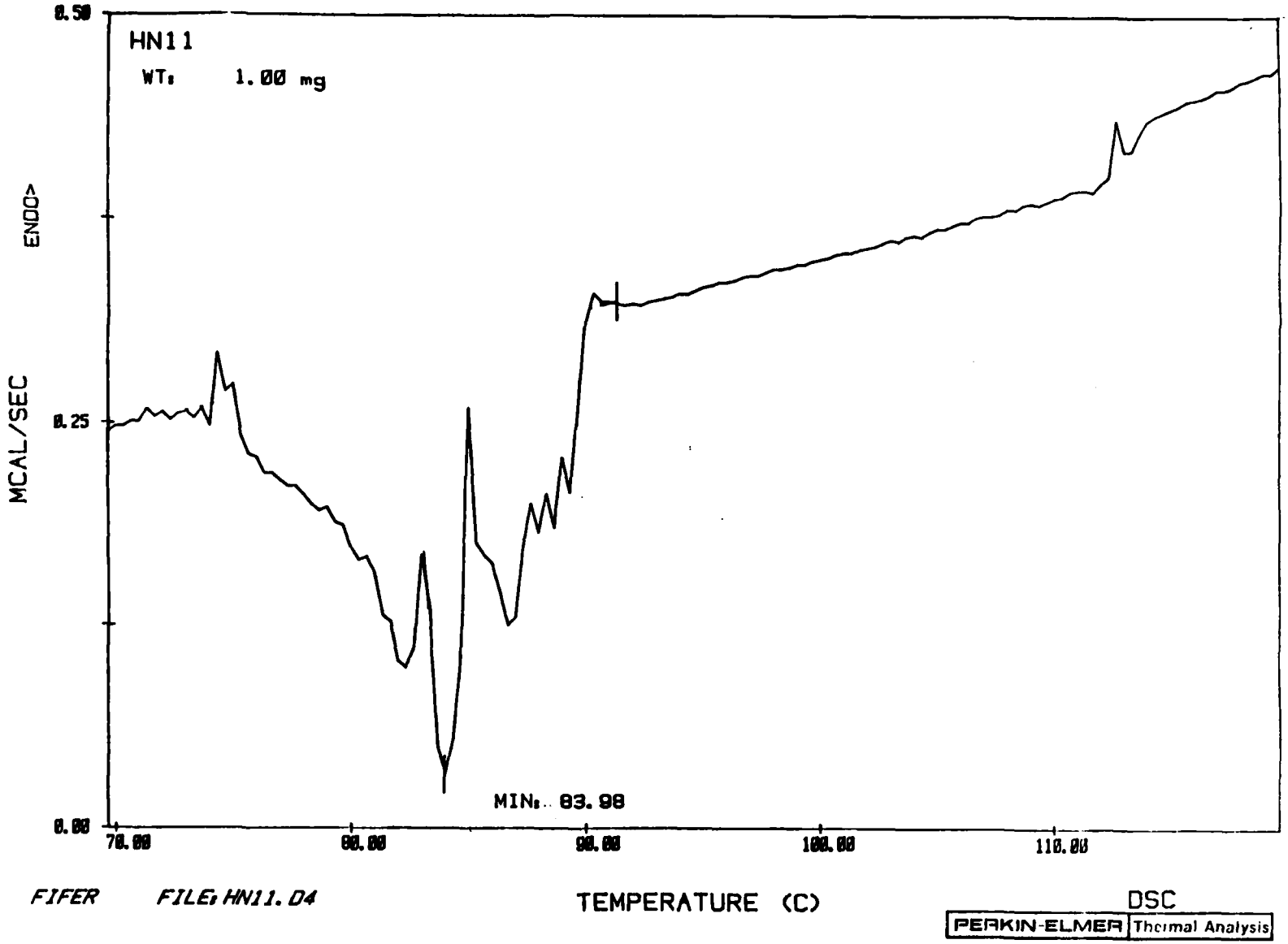

Figure 4. Representative Thermogram Showing Jagged Exotherms Obtained with HAN Confined to Narrow-Bore Stainless Steel Tubing. The various peaks Probably are Indicative of Sample Degassing and in Some Instances, Possible Movement of the Stainless Steel Tubing.

suggesting that the propellant was not compatible with the tubing. The simplicity of this technique, and the fact that several samples could be run simultaneously, suggest that it perhaps deserves further evaluation, using microbore tubing of some other material.

C. Samples in Pressurized DSC

An alternative to confinement for suppression of water vaporization and boiling is instrument prepressurization. Although confinement techniques like that described above can produce higher pressures than are practical using prepressurization, prepressurization has some potential advantages: any kind of sample container can be used that is normally used at atmospheric pressure (metal pans with swaged on lids need to be pierced to prevent collapse during instrument pressurization), and there are no stringent requirements as far as precise control of loading density, avoidance of bubbles, removal of dissolved gases, etc., as for highly-confined samples. Makeshift techniques for pressurizing the DSC were used at first: simple valves were used to restrict the purge gas flow exiting the sample and reference chambers, and a large pile of lead bricks was placed on the cover plate to assist the standard hold-down mechanism. A number of experiments were carried out at 0.76 MPa (110 psi), using pierced aluminum pans. The results were very encouraging; although the initiation temperatures (T_{in}) still varied from run to run, multiple exotherms were eliminated, and in almost every case no pre-endotherms were observed (see Table 1B). In addition, there seemed to be a correlation between sample loading and temperature (Table 1B). A regression analysis of the results for NOS indicated that the temperature increased linearly with sample loading. This relation did not hold for samples run under any of the conditions described previously. These preliminary experiments were sufficiently promising that the DSC was subsequently modified for pressure operation at up to 6.9 MPa (1000 psi), as described in the experimental section above and in detail in Reference 4.

Results at 6.9 MPa (1000 psi) were found to be even more reproducible; peak shapes at this pressure are very reproducible, although there is still considerable variation in the T_{in} of the HAN samples. This occurred in spite of the fact that all samples were kept at the same loading density (3.1 ± 0.1 ug). However, the reproducibility for 1845 significantly improved with an average temperature of 120°C and standard deviation of only 4.0°C (Table 1B). Unfortunately, a rather small number of samples were treated in this manner and thus more work needs to be done with inert sample pans. Figures 5 and 6 show typical thermograms for 1845 and 13 M HAN, respectively, in pierced aluminum pans. No endotherms are observed prior to initiation; in fact, there is no sign in the baseline of any kind of reaction prior to initiation. For 1845 in metal sample pans at 6.9 MPa, there is a single exotherm. (The weak endotherm immediately following the exotherm in Figure 5 is probably not real, but due to re-equilibration of the instrument following initiation.) For 13 M HAN, the initiation exotherm is followed by a broader secondary exotherm at somewhat higher temperatures, as shown in Figure 6. Apparently, initiation of HAN leads to a residue, which then subsequently undergoes further reaction. It may be that this product is simply aluminum nitrate, which decomposes to 150°C, however, further work is necessary to determine this. If this were the case, its absence when 1845 is analyzed could be explained by the fact that 1845 is stochiometric and the nitrate is completely consumed in the

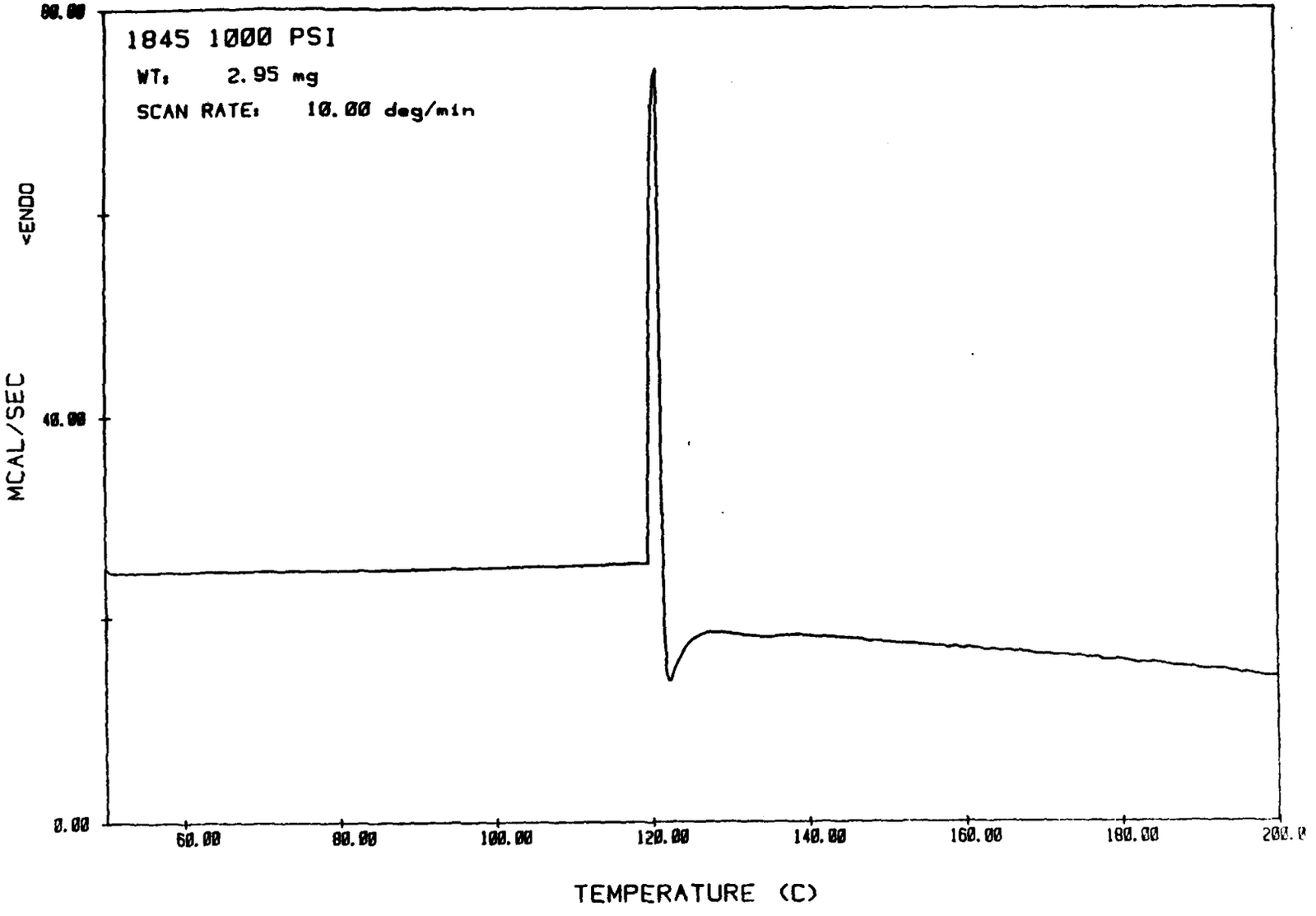

Figure 5. Thermogram for Low Stability Sample of 1845 in Pierced Aluminum Pan at 6.9 MPa (1000 psi), Showing Absence of Pre-Endotherms, and Reproducible Peak Shapes for Prepressurized Samples

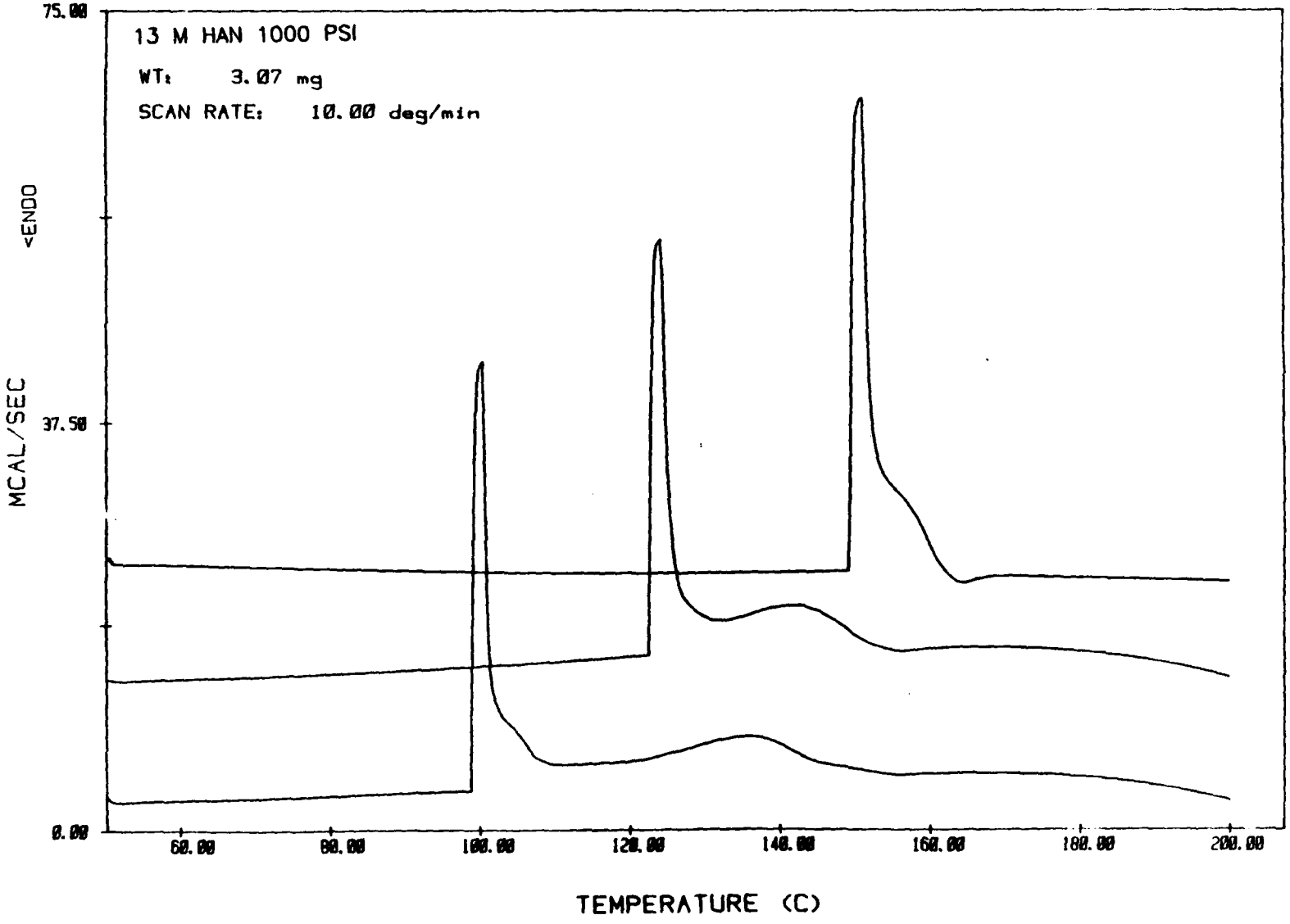

Figure 6. Thermograms for Three Samples of 13 M HAN at 6.9 MPa (1000 psi), Showing Second Exotherm Due to Formation of Ignition Residue

decomposition. If the HAN ignites at an abnormally low temperature (Figure 6), the separation between the primary and secondary exotherms increases; conversely, for more stable samples of HAN with higher T_{in}, the secondary exotherm is observed as an unresolved shoulder on the high temperature side of the main initiation exotherm. Even after heating aqueous HAN to 200°C and cooling, a residue remains that corresponds to about 15% of the initial weight of HAN; for the propellant 1845, on the other hand, complete reaction occurs at initiation, and no residue is found after the experiment.

In the same time frame in which the 6.2 MPa (1000 psi) experiments were performed another series was also run at 5.2 MPa (750 psi) using either Al or Ta pans. (Tantalum is believed to be inert to HAN-based materials.) The T_{in}s obtained using Al pans still show significant scatter, however the reproducibility for the Ta samples is the best obtained yet (see Table 1B), with a variance of only 2.4°C. Although a relatively small number of samples were analyzed in the Ta pans, the results are promising enough to pursue the concept of using pre-pressurization and containers which are totally inert.

IV. SUMMARY

Basic physical phenomena and technical problems involved in using a DSC to measure the relative decomposition temperature of liquid propellants have been outlined. Although the procedures have been obtained for liquid propellants, they may be useful in other areas as well. The main problems to be overcome in the liquid propellant system include the following which manifest themselves as numerous and variable T_{in}s in the DSC traces:

a. Reactivity of the propellant with the instrumental/sampling materials.

b. Spreading and splattering of the propellant prior to reaction.

c. Irreproducible vaporization as the experiment progresses.

The first problem can be minimized by selecting materials which are compatible with the propellant. However, in the case of the LP materials this is not a simple matter and care must be taken so that no metal from the equipment or supplies contaminates the samples, including sample pans as well as syringe needles, etc. Partial success was obtained by using sample pans coated with Au and Pt (atmospheric conditions); however, T_{in}s are still widely varying. More work has been done in both selecting sample containers and pre-treating sampling materials.

The second problem, sample splattering, has also been addressed in this work. This also results in numerous endotherms and exotherms being obtained and in the case of LPs, can be minimized by dispersing powders and fibers into propellants. In most cases, this seemed to be effective in eliminating all but the major exotherm, probably due in part to minimizing splatter. However, occasionally runs were obtained with multiple peaks and, in general, the T_{in}s are not reproducible.

The final effect, vaporization suppression, may be the most critical in obtaining reproducible T_{in}s. Preliminary attempts to achieve this have

included self-pressurization (e.g., small samples in containers with little dead volume) and external pressurization (instrumental pressurization). DSC curves from the former method have quite jagged exotherms, possibly due to vibrations of the sample container and/or degassing under the extremely high pressures which arise from strict confinement of the sample in such a small volume. Thus, instrument pressurization has shown the most promise and initial results yielded single exotherms with very regular shape. However, T_{in}s are still variable and lie in the range of 110 to 190°C. Further work has also been done using high pressure and a variety of sampling techniques for which T_{in}s are statistically reproducible. Preliminary results with Ta pans resulted in the most reproducible results yet, with an average T_{in} of 124.7°C and variance of 2.4°C. Thus, the control of vaporization and splattering, combined with the use of inert materials has shown promise for the use of the DSC as a stability test for liquid propellants alone as well as spiked with metals.

The control of vaporization is critical for any liquid sample run in the DSC and it is seen that instrument pressurization is useful in reducing vaporization and therefore improving reproducibility. Sample size and shape is important also and care should be taken to accurately measure the sample and to reproducibly deposit the sample each time to ensure that the drop size is constant. For samples that tend to splatter, the inert substrates such as those previously mentioned might be used to minimize this effect. However, as was pointed out above, if the splattering is due to the escape of decomposition gases (and not simply to deaeration), then reproducibility might be limited by such decomposition and the inert substrates may not be so helpful.

One final point should be noted. The purpose of this work is to obtain conditions for which reproducible T_{in}s for HAN-based samples are obtained. This work has shown that slight variations in sampling or DSC conditions can result in widely varying T_{in} values. Thus, it is essential to select one set of conditions as the reference from which the relative stability of the propellants can be determined. The T_{in}s should reflect the relative stability of samples of differing composition (formulation, impurity and degradation level, etc.). No attempt is made to extrapolate the initiation temperature of bulk quantities of HAN under storage, handling or gun conditions from the T_{in} obtained with milligram quantities of propellants decomposed under the unique conditions of the DSC. The DSC T_{in}s are potentially a reliable indicator of the stability of HAN based liquid propellants and the authors propose nothing more.

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